PROCESS FOR PLASTICIZING POLYVINYL ALCOHOL

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Abstract of **GB1410744**

1410744 Plasticizing polyvinyl alcohol HOE- CHST AG 10 Jan 1974 [20 Jan 1973] 01181/74 Heading C3P Polyvinyl alcohol is plasticized by mixing a polyvinyl alcohol gel containing methanol, with a plasticizer, and subsequently removing the methanol. Methanol containing PVA gels may be obtained by the methanolysis of polyvinylacetate, the separation of the formed methyl acetate therefrom, and then washing with methanol. The methanol content is preferably 40-85 wt. per cent. Plasticizers specified are glycerol, pentaerythritol, sorbitol, ethylene glycol, propylene glycol, butylene glycol, trimethylol propane or a polyethylene glycol having a molecular weight up to 400.

polyvinyl alcohol particles more quickly than into the dry particles, so that uniform distribution of the plasticizer in the polyvinyl alcohol particles is achieved in a relatively short time.

Especially suitable for the process of the invention are polyvinyl alcohols which are prepared by a continuous process, in which a polyvinyl alcohol gel band is cut into pieces and washed with methanol. A process of this kind is described, for example, in German Offenlegungsschrift No. 1,720,709. The methanol is preferably eliminated from the plasticized polyvinyl alcohol by drying. Drying in the presence of the plasticizer must be carried out with constant movement of the dry material so that caking of the plasticized polyvinyl alcohol cannot occur in any part of the dryer. As devices for drying the polyvinyl alcohol gel in the presence of plasticizers, preferably long-time dryers may be used, for example ladle, rotary tube, paddle and bundle-type dryers. The dryers should be designed in such a way that any possible caked dry product can be scraped or beaten off. The usual jacket heated agitator vessels, for example with anchor agitators or planetary mixer can also be used for the process of the invention. The drying itself is carried out at a temperature of from 50 to 130°C at a normal pressure preferably in a nitrogen stream while recovering the methanol. In the case of batch drying of the methanol-containing plasticized polyvinyl alcohol powder or granules the process is carried out preferably first at normal pressure and at approximately 90°C and residual methanol is removed subsequently at a pressure reduced to approximately 12 mm Hg.

All known polyvinyl alcohol plasticizers have boiling points of above 250°C and, therefore, very low vapour pressures, so that they do not evaporate during the drying process nor do they form any low-boiling azeotropic mixtures with methanol.

Polyvinyl alcohols plasticized according to the process of the present invention can be processed thermoplastically into water-soluble solvent-resistant tubes, sheets, films, sealings or injection-moulded articles of all types.

The following Examples illustrate the invention, the parts and percentages being by weight unless stated otherwise.

EXAMPLE 1:

The apparatus used consisted of an agitator vessel with planetary mixer (30 rpm), a jacket for heating and cooling with water, a vacuum connection, a device for producing a superimposed nitrogen atmosphere and a fractionating column.

3800 Parts of methanol-containing polyvinyl alcohol gel granules with a methanol content of 73.7% were used, with the following data measured on the dry polyvinyl alcohol:

viscosity of a 4% aqueous solution	4 cP
degree of hydrolysis	88 mol %

Under a nitrogen atmosphere, moist 200 parts of trimethylol propane and 3 parts of calcium stearate were introduced gradually into the polyvinyl alcohol while stirring quickly.

The contents of the vessel were heated while stirring to 80 to 90°C, and the major portion of the methanol contained in the polyvinyl alcohol was distilled off in approximately 2 hours. Residual methanol was removed at 70°C by reducing the pressure in the vessel to approximately 20 mm Hg during approximately 10 minutes.

After cooling, plasticized polyvinyl alcohol granules of excellent homogeneity were obtained showing a flow curve A seen from the accompanying drawing which was measured in capillary viscometer at 170°C, and from which the good thermoplasticity of the product can be seen. When moulding the material transparent, homogeneous, soft sheets were obtained.

COMPARATIVE EXAMPLE 1:

In the same apparatus as described in Example 1 the following ingredients were introduced

1000 Parts of the same polyvinyl alcohol, but in a previously dried form, which
200 parts of trimethylol propane and
3 parts of calcium stearate, and the mixture was stirred for approximately 2 hours and heated to 90°C.

After cooling the mixture polyvinyl alcohol granules were obtained in which the plasticizer had penetrated only superficially into the polyvinyl alcohol particles, so that measurement of the melt viscosity in the capillary viscometer was impossible with this product. Pressed sheets of this material were brittle and very unhomogeneous.

EXAMPLE 2

In the same apparatus as in Example 1 the following ingredients were introduced at room temperature:

2880 Parts of a methanol-containing granular polyvinyl alcohol gell with a methanol content of 65.3% with the following data measured on dry polyvinyl alcohol:
viscosity of a 4% aqueous solution: 18 cP,
degree of hydrolysis: 88 mol %,
100 parts of trimethylol propane,
30 parts of polyethylene glycol, molecular weight 1500, as lubricant.

Under a nitrogen atmosphere, the mixture was heated while stirring continuously at a jacket temperature of 95°C, and the methanol was distilled off. Residual methanol was removed at 80°C by evacuating to approximately 20 mm Hg during 10 minutes.

The plasticized polyvinyl granular alcohol obtained after cooling still contained from 4 to 5% of methanol and was of excellent homogeneity, as could be seen from the moulding of the material into a transparent sheet. The accompanying drawing shows the flow curve B measured in a high-pressure capillary viscometer at 200°C from which the good thermoplastic mouldability of the product can be derived.

COMPARATIVE EXAMPLE 2:

In the same apparatus as in Example 1 the following ingredients were introduced at room temperature:

1000 Parts of the same polyvinyl alcohol as in Example 2, but dried to a solids content of approximately 95%,
100 parts of trimethylol propane,
30 parts of polyethylene glycol, molecular weight 1500, as lubricant.

The mixture was stirred for approximately 2 hours and heated at a jacket temperature of approximately 95°C.

A sample of the product obtained after cooling could not be measured in the high-pressure capillary viscosimeter; compressed sheets manufactured from the product were only loosely sintered, inhomogeneous and very brittle.

WHAT WE CLAIM IS:—

1. A process for plasticizing polyvinyl alcohol which comprises mixing a methanol-containing polyvinyl alcohol gel with a plasticizer and removing the methanol.

2. A process as claimed in claim 1, wherein the methanol-containing polyvinyl alcohol gel is obtained by methanolysis of polyvinyl acetate, separating the methylacetate formed from the polyvinyl alcohol, and washing the latter with methanol.

3. A process as claimed in claim 1 or claim 2, wherein the moist polyvinyl alcohol or the polyvinyl alcohol gel has a methanol content of from 40 to 85% by weight.

4. A process as claimed in claim 1 carried out substantially as described in Example 1 or Example 2 herein.

5. A plasticized polyvinyl alcohol whenever obtained by a process as claimed in any one of claims 1 to 4.

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1410744 COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale